

Diadochite from the Hinomaru-Nako Mine, Yamaguchi Prefecture, Japan

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Abstract Diadochite from the Hinomaru-Nako mine occurs as an efflorescence on goethite-stained cracks of andalusite-pyrophyllite-quartz ore including pyrite, augelite, trolleite, scorzalite and other aluminum phosphates. It is colorless to pale beige in color with vitreous luster. The representative chemical analysis by EPMA gave Fe₂O₃ 38.46, Al₂O₃ 0.33, SO₃ 19.78, P₂O₅ 17.06, Total 75.63 wt.%, yielding the empirical formula (Fe_{1.97}³⁺Al_{0.03})_{Σ2.00}(PO₄)_{0.99}(SO₄)_{1.01} on the basis of O=8.5 in anhydrous part. The X-ray powder diffraction pattern by a Gandolfi camera is indexed on triclinic cell with $a=9.59(1)$, $b=9.74(1)$, $c=7.33(1)$ Å, $\alpha=98.7(1)^\circ$, $\beta=107.9(1)^\circ$, $\gamma=63.9(1)^\circ$.

Key words: diadochite, chemical composition, X-ray data, aluminum phosphates, Hinomaru-Nako mine

Introduction

Diadochite, Fe₂³⁺(PO₄)(SO₄)(OH)·5H₂O, is a typical secondary mineral in phosphorous sedimentary rocks (e.g. Van Tassel, 1985) and metallic ore deposits (e.g. Walenta, 1997). It was originally named for amorphous form of Fe₄[(OH)₄|(PO₄,SO₄)₃]·13H₂O, but another name, destinezite, was used for crystalline diadochite. Dana (1892) regarded the two as synonymous and accepted the name diadochite due to its priority. Though Palache *et al.* (1951) suggested diadochite to be triclinic, the actual triclinic cell parameters were confirmed for the material from Eureka, Nevada, USA over fifteen years later (ICDD 12-209). Recently, the crystal structure of destinezite (“diadochite”) from the soil and weathered bedrock at Alum Cave Bluff, Sevier County, Tennessee has been reported as triclinic, space group *P*1, although its ideal formula is Fe₂³⁺(PO₄)(SO₄)(OH)·6H₂O (Peacor *et al.*, 1999).

At the outcrop of hydrothermally altered acidic tuff of the Hinomaru-Nako mine, Abu Town, Yamaguchi Prefecture, Japan, the third author has recognized a colorless to pale beige-colored efflorescence on goethite-stained surfaces of ore cracks. The X-ray and chemical studies have confirmed it to be diadochite as the first occurrence in Japan.

Occurrence

The present diadochite was collected from the West pit of the Hinomaru-Nako mine located about 1 km east of Kiyō station of San'in Line. The ore deposits are developed in hydrothermally altered acidic tuff and the ores are composed mainly of andalusite, phyllophylite and quartz with minor topaz, diaspore and a kaoline mineral. The detailed geology around the area (Kamitani, 1977) and mineralogy on principally aluminum phosphates including augelite, trolleite, scorzalite, svanbergite, florencite-(Ce), gorceixite, goyazite, gatumbaite-like mineral and variscite (Matsubara & Kato, 1998) have been reported, respectively.

The aluminum phosphates occur especially in the coarser-grained andalusite-rich ores in association with pyrite. Pyrite is developed as spotted aggregates filling voids or minute veinlets in the ore. At many voids where pyrite was dissolved and weathered out by groundwater, well crystal forms of andalusite, trolleite-augelite pseudomorph after possibly berlinite, and scorzalite are observed. Along the cracks of aluminum phosphates and pyrite-rich ores brownish goethite stains cover at the outcrop and dump.

Diadochite (NSM M-27912) is found as an efflorescence on those goethite-stained surfaces of ores (Fig. 1). The thickness and dimension of the efflorescence are under 1 mm and 50×40 mm, respectively. It is colorless to pale beige in color with vitreous luster. The aggregates composed of very minute crystals are very fragile. The crystals are short pseudo-rhombic prisms up to 10 μm in width and 20 μm in length (Fig. 2). The cell parameters suggest that the crystal is elongated [001] and well developed prism faces are {100} and {010}.

Chemical Composition

Chemical analyses were made by using Link Systems energy dispersive X-ray spectrometer (QX 2000) for all elements except H₂O. The standard materials and detailed analytical procedure have been reported by Yokoyama *et al.* (1993). Distinct chemical heterogeneity was not observed under the examination of BEI photograph (Fig. 3). The results are given in Table 1. Aluminum content is very small in general or is under the detection limit at most analytical points. No. 1 analysis in Table 1 is close to the theoretical figures, Fe₂³⁺(PO₄)(SO₄)(OH)·5H₂O, except minor component of Al. Therefore, the empirical formula in addition with estimated H₂O by difference, (Fe_{1.97}³⁺Al_{0.03})_{Σ2.00}(PO₄)_{0.99}(SO₄)_{1.01}(OH)_{0.99}·5.05H₂O on the basis of O=8.5 in anhydrous part, corresponds to the ideal formula. The other analyses, however, are slightly excess H₂O than the ideal figure. The ideal formula derived from the crystal structure analysis by Peacor *et al.* (1999) requires 6H₂O, but almost previously reported analyses exist in the range of 5 to 6H₂O as like the present analyses. The composition of Hinomaru-Nako mine diadochite is characterized by a little trend

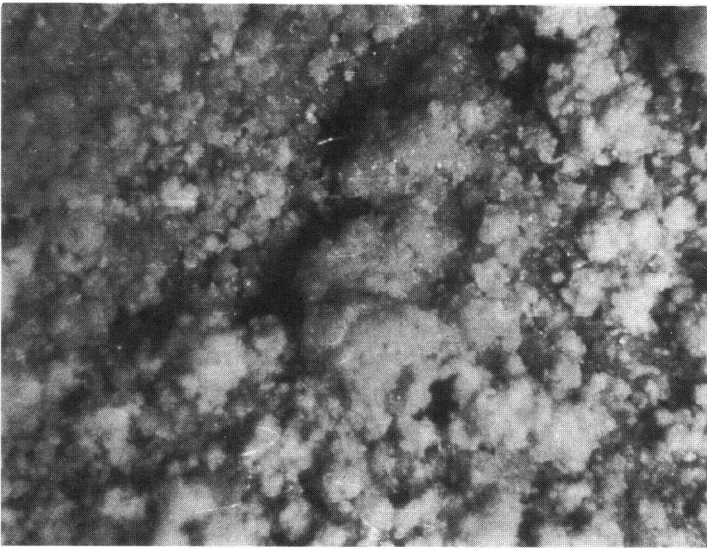


Fig. 1. Photomicrograph of diadochite. Field view, approx. 7×9 mm.



Fig. 2. SEM photograph of the aggregate composed of diadochite (prismatic crystals) and possibly kaoline minerals (platy crystals).

Table 1. Chemical analyses for diadochite from the Hinomaru-Nako mine. 1, 2 & 3: Hinomaru-Nako mine. 4: the ideal value for $\text{Fe}_2(\text{PO}_4)(\text{SO}_4)(\text{OH}) \cdot \text{H}_2\text{O}$. n.d.: not detected.

	1	2	3	4
Al_2O_3	0.33	n.d.	n.d.	0
Fe_2O_3^*	38.46	39.16	38.23	38.97
P_2O_5	17.06	16.76	16.84	17.32
SO_3	19.78	19.41	20.03	19.53
H_2O	24.37**	24.67**	24.90**	24.18
Total	100.00	100.00	100.00	100.00
O=8.5 in anhydrous part				
Al	0.03	0	0	0
Fe	1.97	2.03	1.97	2
P	0.99	0.98	0.98	1
S	1.01	1.00	1.03	1
H	11.08	11.33	11.39	11

*: total Fe. **: by difference.

of $(\text{SO}_4)^{2-} > (\text{PO}_4)^{3-}$.

X-ray Crystallography

The preliminary X-ray powder diffraction pattern was obtained by the diffractometer, but it included minor impurity with a reflection peak, $d=7.17 \text{ \AA}$, corresponding to the strongest one of kaoline mineral. The detailed X-ray powder diffraction data was taken by a 114.6 mm Gandolfi camera using Cu/Ni radiation under 34 kV, 34 mA and 7 days. The diffraction data are essentially same as those of the material from Vysocany, Prague, Czecho (ICDD 42-1364) (Table 2). The unit cell parameters calculated from the present data are: $a=9.59(1)$, $b=9.74(1)$, $c=7.33(1) \text{ \AA}$, $\alpha=98.7(1)^\circ$, $\beta=107.9(1)^\circ$, $\gamma=63.9(1)^\circ$. These are very close to those from Vysocany, $a=9.584$, $b=9.748$, $c=7.3380 \text{ \AA}$, $\alpha=98.78^\circ$, $\beta=108.00^\circ$, $\gamma=63.869^\circ$, but are slightly larger than those from Alum Cave Bluff, $a=9.570(1)$, $b=9.716(1)$, $c=7.313(1) \text{ \AA}$, $\alpha=98.74(1)^\circ$, $\beta=107.90(1)^\circ$, $\gamma=63.86(1)^\circ$ derived from the crystal structure analysis by Peacor *et al.* (1999).

Discussion

The ore from the Hinomaru-Nako mine including many phosphorous minerals and pyrite has been formed under the hydrothermal alterations. The occurrence of pyrite and such sulpho-phosphate as svanbergite indicates that phosphoric and also sulphuric activities have participated in the alteration processes. On the other hand,

Table 2. X-ray powder diffraction data for diadochite.

Hinomaru-Nako				Vysocany		Hinomaru-Nako				Vysocany	
hkl	d _{obs.}	d _{calc.}	I	d	I	hkl	d _{obs.}	d _{calc.}	I	d	I
010	8.75	8.75	s	8.77	85	$\bar{3}\bar{1}2$	2.73	{2.73 2.72}	wb	2.731	6
100	8.29	8.29	s	8.27	84	$\bar{3}\bar{3}1$				2.718	11
110	7.88	7.88	vw	7.89	15	$\bar{3}\bar{2}2$				2.698	5
001	6.97	6.97	vw	6.98	7	031				2.671	1
$\bar{1}\bar{1}1$	6.12	6.13	w	6.143	14	$\bar{2}12$					
0 $\bar{1}1$	5.50	5.50	vw	5.505	29	330	2.62	2.63	w	2.628	1
011	5.41	5.40	vw	5.402	15	232	2.60	{2.60 2.60}	w	2.600	15
$\bar{1}10$	5.06	5.05	w	5.054	22	231					
120	4.78	4.78	w	4.780	5	$\bar{2}20$	2.53	{2.53 2.52}	vw	2.526	7
101	4.73	4.74	w	4.737	24	$\bar{3}02$					
111	4.62	4.63	vvw	4.630	8	$\bar{2}21$				2.502	2
210				4.554	2	321	2.46	2.47	vvw	2.467	3
$\bar{2}\bar{1}1$				4.492	2	$\bar{3}\bar{3}2$				2.448	1
020	4.37	4.37	vs	4.375	100	$\bar{1}30$					
200	4.14	4.15	vw	4.141	14	$\bar{1}03$	2.42	2.42	vw	2.415	7
$\bar{2}01$	4.08	4.08	vs	4.083	69	$\bar{2}\bar{1}3$				2.392	5
$\bar{2}\bar{2}1$	3.93	3.93	vvs	3.930	97	$\bar{4}\bar{2}1$					
1 $\bar{1}1$				3.821	1	202				2.369	4
0 $\bar{2}1$	3.74	3.74	vw	3.738	12	301	2.36	{2.36 2.36}	vw	2.358	4
021				3.673	5	$\bar{1}31$					
121	3.64	3.65	w	3.653	18	003				2.326	3
$\bar{1}02$	3.58	{3.58 3.57}	w	3.582	9	222	2.31	2.32	vw	2.313	7
$\bar{1}\bar{1}2$						122				2.305	3
002	3.49	3.49	m	3.488	27	$\bar{3}41$				2.287	2
211				3.367	2	$\bar{4}\bar{3}1$	2.269	{2.275 2.265}	wb	2.266	9
$\bar{1}20$				3.336	4	$\bar{1}\bar{3}1$					
0 $\bar{1}2$				3.261	3	0 $\bar{1}3$	2.255	{2.257 2.253}	vw	2.258	9
$\bar{2}11$	3.22	{3.22 3.20}	m	3.214	35	$\bar{1}\bar{2}3$					
201				3.199	17	$\bar{1}13$			2.249	4	
$\bar{1}21$	3.13	3.13	w	3.125	17	013				2.236	4
221	3.09	3.09	m	3.083	28	410					
$\bar{3}\bar{2}1$	3.07	{3.08 3.06 3.06}	m	3.062	22	340				2.227	5
230						032			2.215	1	
$\bar{1}\bar{3}1$						$\bar{2}22$					
310				3.019	2	$\bar{4}\bar{1}2$				2.204	1
102	2.94	2.94	s	2.942	80	$\bar{3}12$					
030	2.92	{2.92 2.91 2.90}	vw	2.915	36	$\bar{3}\bar{1}3$				2.194	2
112				2.904	13	141		2.182	7		
$\bar{1}\bar{2}1$						$\bar{3}\bar{2}3$					
$\bar{3}01$	2.85	2.85	w	2.844	14	430				2.168	2
131	2.78	2.78	vw	2.779	8	$\bar{2}\bar{1}2$					
300				2.758	2	$\bar{4}01$				2.151	2

Table 2. (Continued).

Hinomaru-Nako			Vysocany			Hinomaru-Nako			Vysocany		
hkl	dobs.	dcalc.	I	d	I	hkl	dobs.	dcalc.	I	d	I
$\bar{3}\bar{4}2$	2.108	2.119	vw	2.122	3	$\bar{2}\bar{5}1$	1.918	1.925	vw	1.9321	4
$3\bar{1}1$		2.100		2.099	10	$\bar{1}40$				1.9253	1
$0\bar{4}1$		2.097				431				1.9155	3
$\bar{3}03$	2.076	2.078	w	2.077	11	$\bar{3}\bar{5}1$	1.872	1.877	vw	1.9110	5
041		2.075				$4\bar{1}1$				1.9025	1
$\bar{1}\bar{4}2$				2.060	2	$\bar{5}\bar{3}1$				1.8877	2
$\bar{4}\bar{4}1$	2.051	2.050	vw	2.051	7	$\bar{3}13$	1.872	1.877	vw		
$\bar{4}02$				2.042	7	$\bar{1}41$				1.8783	4
023				2.036	4	150					
$\bar{2}30$	2.007	2.005	w	2.0203	4	$\bar{5}\bar{2}2$	1.808	1.812	vw	1.8679	9
$\bar{2}31$				2.0048	11	$\bar{1}\bar{5}1$				1.8525	3
$1\bar{1}3$				1.9973	9	213					
421				1.9894	2	042	1.833	1.827	vw	1.8364	2
$\bar{3}20$						$0\bar{3}3$					
440				1.9702	3	$1\bar{2}3$				1.8277	5
$\bar{4}\bar{4}2$				1.9634	1	$\bar{3}\bar{5}2$	1.807	1.807	vw	1.8144	1
411						$\bar{5}\bar{1}2$				1.8071	5
123				1.9576	2						
$\bar{4}\bar{2}3$											
$1\bar{3}2$				1.9459	2						

Hinomaru-Nako: a 9.59(1), b 9.74(1), c 7.33(1) Å, α 98.7(1), β 107.9(1), γ 63.9(1)°. Vysocany: a 9.584, b 9.748, c 7.3380 Å, α 98.78, β 108.00, γ 63.869° (ICDD 42-1364).

diadochite is distinctly found as a secondary mineral with goethite through alteration of primary phosphates and pyrite by weathering at outcrop. The present diadochite includes minor Al due to the source of such high-aluminum minerals as trolleite, augelite, scorzalite and andalusite etc. No other secondary phosphates or sulphates have been observed, but scarce kaoline mineral in association with diadochite was recognized on the SEM photographs and preliminary X-ray powder diffraction data. The genesis of this kaoline mineral, however, is uncertain whether they are acutual secondary minerals or minute fragments derived from the ore.

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